bonded to each other, leave holes for the gas molecules which presumably interact through London forces with the atoms on the inner surface of the holes. Recently Heidt and Johnson[31] have discussed the behavior of oxygen dissolved in water and suggested the existence of two definite hydrates having water molecules hydrogen bonded to oxygen.

In principle the variation of $\Delta\bar{C}_p{}^0$ with temperature could be used to distinguish between a two-hydrate model and a more complex "gas-hydrate like" or "iceberg" type of model. In practice no decision can be made for chlorine. The chlorine hydrolysis data can just barely be fitted by a two-hydrate model, assuming fixed heat capacities for the hydrates. Equally well $\Delta\bar{C}_p{}^0$ could be constant over the whole temperature range, corresponding to a continuous breakdown of a more complex structure. The oxygen solubility data, which cover a larger temperature interval, can be fitted by a two-hydrate model except near 100°, and of course can be fitted by more complex models.

The appreciable changes in the spectrum of Cl_2[7] and O_2[31] on dissolution in water might indicate a specific interaction with one (or a small number of) water molecule. The similarity in behavior of all inert gases, however, would argue for a more general "iceberg" or "gas-hydrate" type of interaction.

Thermodynamic Functions.—From the hydrolysis equilibrium it is possible to calculate a number of thermodynamic quantities which are not presently tabulated in the literature. These quantities are shown in Table IV. The Cl_2(aq) data were obtained from the solubility[24] of chlorine in water (corrected for hydrolysis) and the temperature coefficient of solubility. The HOCl values were then obtained using the present hydrolysis data. A value of −29.7 kcal. for $\Delta\bar{H}_f{}^0$ of HOCl at 18° also was calculated and found to be in good agreement with the calorimetrically measured value of −29.8 kcal.[32]

TABLE IV

THERMODYNAMIC FUNCTIONS OF CHLORINE COMPOUNDS

Temperature, 298.16°K.

	$\Delta\bar{F}_f^0$ (kcal./mole)	$\Delta\bar{H}_f^0$ (kcal./mole)	$\bar{S}^0$ (e.u.)
Cl_2(aq)	1.656	−6.16	27.1
HOCl	−19.040	−29.39	32.0
ClO^-	−8.858	−25.94	9.5

The ClO^- data were calculated using Ingham and Morrison's value[33] for the ionization constant of HOCl at 18° and the value for the heat of ionization at 18°.[32] Both values were corrected to 25° using Pitzer's equations[34] for the effect of temperature on the ionization of oxygenated acids.

Acknowledgment.—This work was performed under the auspices of the U. S. Atomic Energy Commission.

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BERKELEY, CALIF.

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORIES, LOUISIANA STATE UNIVERSITY]

The Stability of $FeCl^{++}$ in Perchlorate Solutions[1]

BY HANS COLL, ROBERT V. NAUMAN AND PHILIP W. WEST[2]

RECEIVED JULY 21, 1958

The stability constants of the species $FeCl^{++}$, formed by complexing chloride ion with a large excess of iron(III), have been determined. This complex exhibits an absorption band around 350 mμ which was used for a spectrophotometric estimation of K_1, the stability constant of $FeCl^{++}$. K_1 was determined by measuring the concentration of the complex at the wave length of maximum absorption at various concentrations of iron(III) in perchloric acid media between 2.5 and 9 *M*. K_1 was found to increase with acidity from a value of 4.2 to 6100. Solutions of sodium and magnesium perchlorate in perchloric acid were also used as solvents in these studies. A plot of log K_1 *vs.* perchlorate ion concentration resulted in separate curves for the acid and the salt solutions. From the change of K_1 with temperature $\Delta H°$ and $\Delta S°$ were determined for solutions of 3.0 and 8.5 *M* perchloric acid. A qualitative explanation for the dependence of the stability of the chloro complex on the composition of the medium is given in terms of the dehydrating action of perchlorates. The formation of iron(III) perchlorate complexes appears to be unlikely.

Introduction

During the development of a spectrophotometric procedure[3] for the quantitative determination of chloride ion by means of iron(III) perchlorate in perchloric acid, it was observed that the intensity of the absorption band of the iron(III) chloro complex, around 350 mμ, increased appreciably with acid concentration. A high excess of iron(III) with respect to chloride ion (about 100:1) was maintained in these experiments. Under these conditions, the exclusive formation of the lowest chloro complex, $FeCl^{++}$, can be assumed in view of previous studies on the stability of iron(III) chloro complexes.[4-6] The sharp increase of light absorption with perchloric acid concentration suggested a pronounced influence of the acid concentration on the stability of the complex $FeCl^{++}$. The primary purpose of our investigation was then

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[1] This investigation was supported by the Office of Ordnance Research, U. S. Army.

[2] Request for reprints should be addressed to Philip W. West.

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to study the dependence of

$$K_1 = \frac{(\mathrm{FeCl}^{++})}{(\mathrm{Fe}^{+++})(\mathrm{Cl}^-)}$$

on the perchloric acid content of the solutions in a concentration range from 2.5 to 9.0 *M*. Values of K_1 at low ionic strengths (<2) have been reported by other investigators.[4-6]

The constant K_1 was evaluated in the following manner. The FeCl^{++} concentration was determined spectrophotometrically. The concentrations of chloride ion and perchloric acid were kept constant for each set of measurements, while the concentration of iron(III) was varied. One can write

$$K_1 = \frac{y}{(a - y)(b - y)} \tag{1}$$

where y is the concentration of FeCl^{++}, a the total concentration of iron(III) and b the total concentration of chloride. In order to simplify eq. 1, $a - y = a'$ may be treated as a constant. Thus, the absorbancy of FeCl^{++} (A), corrected for background absorption due to Fe(III) by means of a reference solution, can be related to a' by the equation

$$A = Ey = E\frac{a'bK_1}{1 + a'K_1} \tag{2}$$

E designates the molecular extinction coefficient of FeCl^{++}. From eq. 2 one obtains

$$1/A = \frac{1}{EbK_1} \times \frac{1}{a'} + \frac{1}{bE} \tag{3}$$

E and K_1 may be determined from the slope (m) and intercept (c) of the straight line which is obtained by plotting $1/A$ *vs.* $1/a'$; thus, $K_1 = c/m$ and $E = 1/(bc)$.

Experimental

Apparatus.—The measurements were performed with a thermostated Beckman Model DU spectrophotometer equipped with a tungsten lamp. The temperature of the cell compartment of the instrument could be controlled within ±0.5°. Matched 1 cm. quartz cells were used.

The vapor pressure of water above perchlorate solutions was compared by means of two Manganin-Advance thermocouples bucking each other for measurements of minute temperature differences. The device has been described in the literature.[7,8] The wires of the thermocouples were sprayed with a plastic insulating material and were coated with paraffin to prevent corrosion. By this method, using only one drop of sample, it was possible to detect a difference in vapor pressure of water above 6.00 and 6.01 *M* perchloric acid, which corresponds to a difference of about 0.03 mm.

Solutions of FeCl^{++} were protected from light by coating the glass containers with black paint.

Solutions.—Standard sodium chloride solutions contained 1000, 500, 200 and 100 mg. of chloride ion per liter.

Iron(III) perchlorate, purified from traces of chloride by repeated extractions with 70% perchloric acid, was dissolved in distilled water, and the solutions were standardized by titration with dichromate. The final concentrations of the stock solutions were adjusted to be 0.522, 0.100, 0.0100, 0.00500 *M* with respect to iron(III), and 2 *M* with respect to perchloric acid.

Perchloric acid (70%, Analytical Reagent, Merck) was stored in a closed system buret protected against moisture by means of drying tubes charged with anhydrous magnesium perchlorate. The acid was standardized against sodium hydroxide.

Sodium perchlorate solution (7.75 *M*) was prepared from the hydrated, reagent grade salt. The solution was standardized gravimetrically by weighing $\mathrm{NaClO_4}$ dried at 170°.

Magnesium perchlorate solution (2.78 *M*) was prepared from the recrystallized anhydrous salt. Trace amounts of an interfering contaminant were removed by washing with small portions of ether. The solution was standardized by titration with ethylenediamine tetraacetate, eriochrome black-T serving as the indicator.[9]

Procedure and Results

In preliminary experiments it was found that the absorption band of the complex FeCl^{++} shifted from approximately 336 to 352 mμ when the acidity of the solution was increased from 2.5 to 9.0 *M*. $E_{\max}$, the molecular extinction coefficient at the wave length of maximum absorption, was determined independently at each acid concentration. In the general procedure for each set of measurements the calculated amount of perchloric acid was delivered to 10-ml. volumetric flasks. Varying amounts of iron(III) perchlorate, a, and a constant amount of sodium chloride, b, were added; the solutions were brought to volume and thermostated. The quantities a and b were adjusted to give optical densities between 0.100 and 0.900, a being always greater than b. The values of a were chosen to give an approximately equal spacing of points in a plot of $1/A$ *vs.* $1/a'$. The iron(III) concentrations were limited to values below 0.05 *M*. For each solution a blank that contained iron (III) perchlorate but no sodium chloride was prepared. All readings were taken with respect to distilled water at the wave length of maximum absorbancy, $\lambda_{\max}$, and for some sets also at some longer wave lengths. The absorbancies were measured after thermal equilibrium had been reached, and the blank values were subtracted. Each set of a certain acidity consisted of about 10 solutions.

The measurements were first taken with solutions of 9 *M* perchloric acid, because it was expected that E_1 at such an acidity would be sufficiently high to allow an estimation of A_L, the limiting absorbancy, which is obtained if, according to eq. 2, $1 + Ka' \approx Ka'$, or when $y = b$. The extent of association at a certain value of a could then be estimated from

$$y = \frac{Ab}{A_L} \tag{4}$$

where A stands for the absorbancy measured at a certain value of a. Then $a' = a - y$ could be calculated with good accuracy, because y was usually considerably smaller than a. A correction of the blank values—the blanks contained a, the samples $a - y$ moles of uncomplexed iron-(III) per liter—was found to be unnecessary. Next, $1/A$ was plotted against $1/a'$. The slope and intercept of the straight line were obtained from the graph, because calculations by the method of least squares were rendered unreliable by difficulties in the assignment of proper weighting factors. An estimate of the precision, admittedly somewhat arbitrary, was made by drawing the two extreme straight lines which could be considered as representing the experimental results. K_1 and E were calculated from the average of these extremes.

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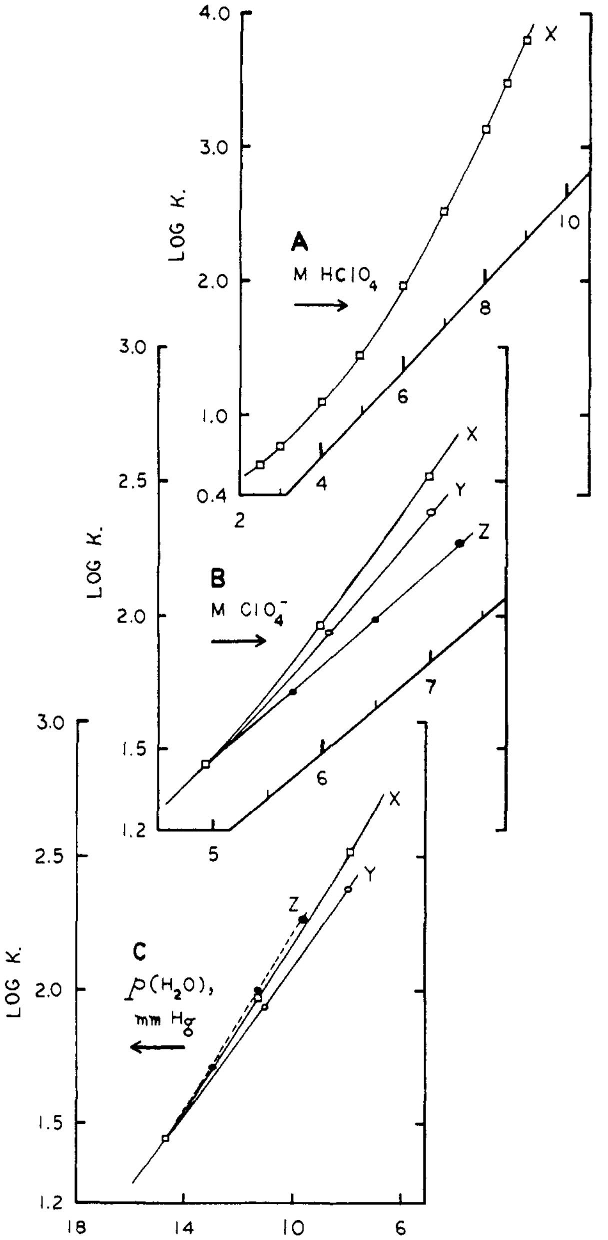

Fig. 1.—A, plot of $\log_{10} K_1$ *vs.* concentration of perchloric acid (25°); B, plot of $\log_{10} K_1$ *vs.* perchlorate ion concentration (25°); C, plot of $\log_{10} K_1$ *vs.* vapor pressure of water above the solutions (25°). Media: curves X, perchloric acid; curves Y, magnesium perchlorate in 4.95 *M* perchloric acid; curves Z, sodium perchlorate in 4.95 *M* perchloric acid.

TABLE I

STABILITY CONSTANTS OF $FeCl^{++}$ (25°)

Medium	$P(H_2O)$, mm.	K_1
	$HClO_4$, *M*	
2.50	20.81	4.2 ± 0.1
3.00	19.89	5.8 ± .1
4.00	17.47	12.5 ± .2
4.95	14.65	28.0 ± .3
6.00	11.21	92 ± 1.2
7.00	7.87	329 ± 4.0
8.00	4.91	1340 ± 25
8.50	...	2960 ± 50
9.00	...	6100 ± 100
	$HClO_4$ (4.95 *M*) plus $NaClO_4$ *M*	
0.775	12.90	52 ± 0.5
1.55	11.25	97 ± 1.4
2.32	9.62	184 ± 3.0
	HClO (4.95 *M*) plus $Mg(ClO_4)_2$ *M*	
0.555	11.02	86 ± 1.2
1.03	7.96	240 ± 5

In the next set of experiments (8.5 *M* acid), the previously determined value of E was employed to estimate y and a'. It was found that within the limits of experimental error, $E_{\max}$ did not vary with acid concentration. Because uncertainty in the graphical evaluation of the intercept became quite appreciable at low acidities, values of $E_{\max}$ which were determined at acidities above 6 *M* were averaged. This value of 2.91×10^3 henceforth was used to establish the intercepts of all plots. This led to insignificant corrections for previously determined values of K_1 above 6 *M*. The linearity of the plots was found to be very satisfactory for readings taken at $\lambda_{\max}$, while some deviations occurred at the other wave lengths. The results are summarized in Table I and Fig. 1A.

Our studies, which had been intended to include other media, had to be limited to perchlorate solutions because other solvents apparently reacted with iron(III); such interactions invariably gave rise to the appearance of intense absorption bands in the same spectral region as the complex $FeCl^{++}$. The constant K_1 was determined in the same manner as outlined above in solutions containing sodium perchlorate and magnesium perchlorate in 4.95 *M* perchloric acid (Table I, Fig. 1B, curves Z and Y). The concentration range of the salts was limited by their solubility in perchloric acid. Slight shifts of the absorption peak toward longer wave lengths were observed for increasing salt concentrations. $E_{\max}$ was the same as the one previously determined. From Fig. 1B it is evident that three separate curves arise if K_1 is plotted against perchlorate ion concentration in moles per liter. An attempt was made to represent all points by a single curve by plotting log K_1 as a function of other variables. A plot of log K_1 *vs.* ionic strength, within the experimental error, made the sodium and magnesium perchlorate values representable by one curve, which, however, had a considerably smaller slope than the one for perchloric acid. The significance of ionic strength at such high concentrations is unknown. Thus, this and other arbitrary scales did not seem to be very helpful toward elucidating the influence of the medium on the activities of the species involved in the iron(III)-chloride equilibrium. It was hoped that new insight could be gained by plotting log K_1 *vs.* the vapor pressure of water above the solutions. For this purpose the vapor pressure of water above solutions of sodium perchlorate and magnesium perchlorate in perchloric acid, which were used as media for the determination of K_1, were compared with the vapor pressure of water above pure aqueous perchloric acid standards. The thermoelectric device used for this purpose measured small temperature differences arising from different rates of evaporation of the unknown and the standard solution. The measurements were performed at 25°. The results were expressed in mm. by comparision with the vapor pressure of solutions of perchloric acid as reported by Pearce and Nelson.[10] The plot of log K_1 *vs.* the vapor pressure of water (Fig. 1C) shows a rearrangement and closer approach of the curves in comparison to Fig. 1B.

For a comparison of thermodynamic data, K_1 was determined at various temperatures between 25 and 45° at perchloric acid concentrations of 3.0 and 8.5 *M*. The change in standard free energy, $\Delta F°$, was calculated from $\Delta F° = -RT \ln K_1$, and $\Delta H°$, the standard enthalpy change, could be evaluated from a plot of log K_1 *vs.* $1/T$ by means of the van't Hoff equation. $\Delta S°$ was calculated from $\Delta F° = \Delta H° - T\Delta S°$. The following results were obtained (25°): in 3.0 *M* acid: $\Delta F° = -1.0$ kcal./mole, $\Delta H° = 3.8$ kcal./mole, $\Delta S° = 16$ e.u.; in 8.5 *M* acid: $\Delta F° = -4.7$ kcal./mole, $\Delta H° = -2.3$ kcal./mole, $\Delta S° = 8.2$ e. u. The lack of agreement among the thermodynamic data reflects the fact that the standard states chosen for the reaction

$$Fe^{+++} + Cl^- \rightleftharpoons FeCl^{++}$$

are not the same in both cases given. It is evident that we have not followed the usual (but in this case impractical) convention for choosing standard states so that activities and molalities are equal in dilute aqueous solutions; by our procedure the standard states are chosen implicitly so that activities and molalities of the Fe^{+++}, Cl^- and $FeCl^{++}$ ions are equal at low concentrations in each acid solution. The solutions are dilute with respect to the Fe^{+++}, Cl^- and $FeCl^{++}$ ions.

Discussion

The belief that the colored species which was made the subject of this investigation actually corresponds to the formula $FeCl^{++}$ was further supported by the linear relation between $1/A$ and $1/a'$. From a general stability constant, K_n, written as

$$K_n = \frac{[FeCl_n]}{[Fe][Cl]^n} = \frac{y}{a'(b-y)^n} \qquad (5)$$

and from $A = Ey$, it can be deduced that such a linear relation is obtained only when $n = 1$. It can further be inferred that only one chloro complex accounted for the observed absorption band.

Extrapolation of the curve in Fig. 1 to an abscissa value of 2 *M* leads to a value of K_1 approximately equal to 3.3. Olerup[5] reported $K_1 = 5.7$ at 20° in 2 *M* perchloric acid; referred to 25° this value would be somewhat higher. Rabinowitch and Stockmayer[4] calculated $K_1 = 5.6$ for the same ionic strength, in fair agreement with Olerup's result, but considerably higher than the extrapolated value from this investigation. These authors determined the stability constant spectrophotometrically, but they did not measure the absorbancy due to $FeCl^{++}$ at λ_{max}. They further did not consider the possibility of a shift of the absorption band with variations of acidity or ionic strength and assumed that the molecular extinction coefficient, at the respective wave lengths, was invariant with the composition of the reaction medium. These factors may possibly account for the disagreement of results. At ionic strengths lower than 2, other authors[11-13] obtained values for K_1 which were smaller than those calculated by Rabinowitch and Stockmayer[2] for the same ionic strengths of the medium.

A qualitative explanation for the remarkable increase of K_1 with perchlorate concentration may be given in terms of the strong dehydrating action of perchlorates. Such a trend can be expected because the combination of iron(III) with chloride ion to give $FeCl^{++}$ must be preceded by a partial removal of the hydration sphere from the reactants. It therefore appears to be more appropriate to write the reaction of iron(III) with chloride ion as

$$Fe(H_2O)_6^{+++} \longrightarrow Fe(H_2O)_5^{+++} + H_2O \qquad (1)$$

$$Cl^-(aq.) \longrightarrow Cl^-\text{ (dehydrated)} \qquad (2)$$

$$Fe(H_2O)_5^{+++} + Cl^-\text{ (dehydr.)} \longrightarrow FeCl(H_2O)_5^{++} \qquad (3)$$

Consistent with the dehydration concept are the observed differences in $\Delta H°$ and $\Delta S°$ at different acidities. It is to be expected that steps 1 and 2 are endothermic, while step 3 is exothermic. Hence it is not surprising that $\Delta H°$ was found to be positive in 3*M* perchloric acid where all the species, presumably, are still extensively hydrated. In 8.5 *M* acid at least partial dehydration of the reactants occurs, and steps 1 and 2 have lost their preponderant influence, which results in a negative value for $\Delta H°$. The value for $\Delta S°$ will be positive for the over-all reaction $Fe^{+++} + Cl^- \rightarrow FeCl^{++}$, because the decrease of total charge leads to a decrease in the order of the dipolar solvent molecules which tend to be aligned by the ions. At high acidities, where a large portion of the solvent molecules is in rigid alignment with perchloric acid, such an effect will become less noticeable. The dehydrating action of perchlorate ion cannot, however, be the only factor responsible for the observed changes in K_1. The log K_1 *versus* vapor pressure of water results shown in Fig. 1 give some support for the dehydration concept and at the same time show that the concept, by itself, is insufficient.

In the opinion of the authors, the findings of this investigation invite some doubt as to the existence of iron(III) perchlorate complexes. Sutton,[14] who estimated the stability constant of the complex $FeClO_4^{++}$ as approximately 0.5, determined this value spectrophotometrically at perchloric acid concentrations between 2 and 7 *M*. The basis for this determination seemed to be a small shift of the iron(III) absorption band as a function of acid concentration. An alternative explanation for this phenomenon may be given by interpreting the spectral changes as being due to variation in the degree of dehydration of ferric ion, instead of in association with perchlorate. A quite analogous shift occurred in the case of the chloro complexes.

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Two points in favor of the dehydration concept should be stated: (1) the chloro complex exhibits an unusual stability at high acid concentrations. Such behavior is to be expected from a partial dehydration of the central atom, which can be considered as a diminished competition of water molecules in the formation of iron(III) complexes. Conversely, formation of perchlorate complexes implies a competition between perchlorate and chloride ions in attaching themselves to the central atom, and it is difficult to see why K_1 should rise so steeply with acidity. (2) A very low solubility of iron(III) perchlorate in 70% perchloric acid was observed. Addition of water greatly enhanced the solubility. The extensive formation of complex ions of the formula $FeClO_4^{++}$ can hardly be reconciled with this observation, while depletion of the hydration sphere of ferric ion would explain the reduced solubility.

BATON ROUGE, LOUISIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

The Deuterium Isotope Effect for a Oxidation–Reduction Reaction between Aquo Ions

BY A. ZWICKEL AND HENRY TAUBE

RECEIVED JULY 30, 1958

The effect of substituting D_2O for H_2O on the rate of the reaction of Cr^{++} with $(NH_3)_5CoOH_2^{+++}$ has been investigated. The specific rate of the reaction of Cr^{++} with $(NH_3)_5CoOH_2^{+++}$ decreases by a factor of 3.8, and of Cr^{++} with $(NH_3)_5CoOH^{++}$ by a factor of 2.6, on making this change in solvent. The second reaction is known to proceed by transfer of oxygen from Co(III) to Cr(II), and the first probably also proceeds by the same mechanism. The decrease in rate is taken to indicate that the O–H bonds in the bridging group are stretched in the activated complex; it is evident that the rate decrease does not necessarily imply transfer of hydrogen from reducing agent to oxidizing agent. The kinetics of the reaction of Cr^{++} with $(NH_3)_5CoOH_2^{++}$ have been reinvestigated, and the data reported previously have been revised in some respects.

It has been suggested[1] that electron transfer between two ions such as Fe^{++}aq. and Fe^{+++}aq. takes place through the agency of a hydrogen atom (or proton and electron) which moves from the coördination sphere of the reducing agent to that of the oxidizing agent. No proof of this kind of mechanism has been advanced, but support for it has been found by its advocates[2,3] in the circumstance that the energetics of activation for a diversity of oxidation–reduction reactions in water are so closely similar. The observation made by Hudis and Dodson[4] that the rate of electron transfer between Fe^{++}aq. and Fe^{+++}aq. decreases (by approximately a factor of 2) when the reaction medium is D_2O rather than H_2O has also been taken[4,5] as evidence in support of the H atom transfer mechanism.

The significance which has been attached to the twofold decrease in rate on H_2O–D_2O substitution is surprising when it is considered that the method has not been calibrated by studying the effect for a reaction of this class of known mechanism. In this paper we report the results of experiments designed to learn the magnitude of this isotope effect for the reaction of two aquo ions which, at least by one path, react by a known mechanism which does not involve hydrogen atom transfer. Experiments have been described earlier[6] on the H_2O–D_2O effect for the reaction

$$(NH_3)_5CrCl^{++} + Cr^{++} \longrightarrow \qquad (1)$$

A decrease in rate by about 30% is observed when D_2O rather than H_2O is the reaction medium. This reaction provides only a partial calibration of the effects to be expected for the H_2O–D_2O solvent change; for complete calibration of the H_2O–D_2O effect to be expected for a bridged activated complex, the bridging group should be OH^- or H_2O. Accordingly we have studied the effect of the H_2O–D_2O solvent substitution on the reaction

$$(NH_3)_5CoOH_2^{+++} + Cr^{++} \longrightarrow \qquad (2)$$

This reaction takes place by the two types of paths commonly observed for oxidation–reduction reactions of aquo ions.

$$\text{Rate} = \underset{\text{Path I}}{k_1(Cr^{++})(ROH_2^{+++})} + \underset{\text{Path II}}{k_2' \frac{(Cr^{++})(ROH_2^{+++})}{(H^+)}} \qquad (3)$$

Oxygen atom transfer by path II, which can be taken as involving the reaction of ROH^{++} with Cr^{++}, is quantitative, and at least some transfer by path I is indicated.[7] Thus the system affords the opportunity of testing the effect of replacing OH^- as bridging group by OD^-, and the comparison of this result with that of Hudis and Dodson[4] for the $FeOH^{++}$–Fe^{++} reaction is of direct interest.

Methods

The rate of reaction was followed spectrophotometrically, in preference to using the titration procedure adopted for the earlier work. The spectrophotometric procedure is preferred not only because of its greater convenience, but because complications in the titration procedure can arise. Apparently the Fe^{++} formed when the reaction mixture is quenched by Fe^{+++} can under certain conditions react with the residual $(NH_3)_5CoOH_2^{+++}$.

The solution of Cr^{++} and the compound $(NH_3)_5CoOH_2^{+++}$ were prepared using procedures in general similar to the earlier ones.

Throughout this paper, the following symbols are used R represents $Co(NH_3)_5$; time, t, is expressed in minutes

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